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814 817 QU

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None

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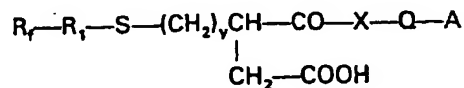
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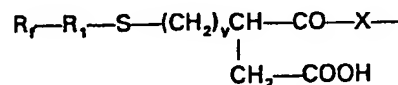
J. A. Kemp & Co

## (54) Fluorinated nonionic surfactants

(57) Perfluoroalkylthio-substituted half esters and amides of succinic acid having the formula



or its isomer, wherein  $R_f$  is perfluoroalkyl,  $R_1$  alkylene, optionally interrupted with oxygen, sulfur or nitrogen atoms,  $x$  is oxygen or  $NH$ ,  $y$  is zero or 1,  $Q$  is a polyether or polyester diradical moiety having a molecular weight of 300 to 5000 or a polysiloxane having 5 to 80 repeating units and  $A$  is hydrogen, hydroxyl, amino, alkoxy, phenoxy, alkylphenoxy, dialkylamino, the group



or its isomer.

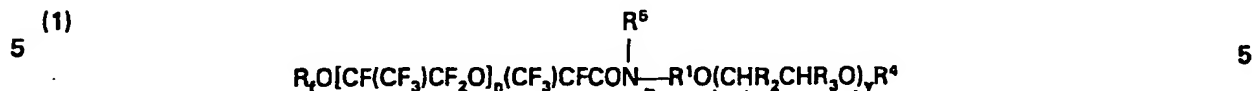
These compounds are prepared by reacting e.g. maleic anhydride with a polyether, polyester, diamine or a polysiloxane derivative of an alcohol or primary amine and then reacting the product with a perfluoroalkyl alkylene thiol. The novel compounds are useful as surfactants with specific applications as wetting agents in coatings, waxes, emulsions, paints and resins.

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## SPECIFICATION

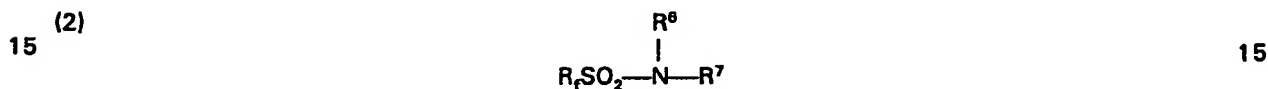
## Fluorinated non-ionic surfactants

U.S. 3,621,059 describes amides derived from hexafluoropropylene oxide polymer acids and polyalkylene oxide having the formula



wherein  $R_1$  is a perfluoroalkyl radical having one to eight carbon atoms,  $n$  is an integer of zero to 100;  $R^1$  is an alkylene radical having two to 12 carbon atoms;  $R^2$  is hydrogen or an alkyl radical having one to four carbon atoms;  $R^3$  is hydrogen or an alkyl radical having one to four carbon atoms, at least one of  $R^2$  and  $R^3$  in each repeating unit being hydrogen;  $y$  is an integer of one to 60;  $R^4$  is hydrogen or an alkyl radical having one to four carbon atoms, and  $R^5$  is hydrogen or an alkyl radical having one to six carbon atoms. These amides function efficiently as surfactants and emulsifying agents. All these surfactants are derived from hexafluoropropylene oxide. 10

US-Patent Specification No. 2,915,554 discloses perfluoro alkanesulfonamides having the formula



In which  $R_1$  is a perfluoroalkyl group having from four to twelve carbon atoms;  $R^6$  is a member of the group consisting of hydrogen, lower alkyl radicals and  $R^6$  and  $R^7$  is a polyoxyalkyl group having the formula



In which  $m$  is an integer from 2 to 3,  $n$  is a number from 2 to about 20, and each  $R''$  is hydrogen or a methyl radical. 20

These sulfonamides serve as surface-active agents. The presence of an  $SO_2$  group is required in all cases.

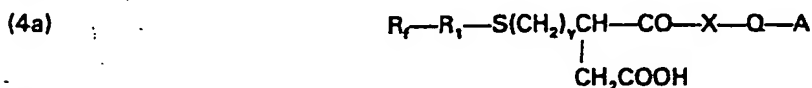
Other nonionic fluorochemical surfactants have been described in German Offenlegungsschriften 2215388 and 2261681. 25

It has now been found that a large variety of useful nonionic fluorinated surfactants can easily be prepared without the necessity of an alkylation reaction and without the need for preparing an intermediate perfluoroalkyl substituted acid, by base catalyzed addition of an  $R_1$ -substituted thiol to the maleic or fumaric half ester or half amide containing a hydrocarbon, polyethylene oxide or polysiloxane group in the ester or amide moiety. It is a further advantage, and contributing to the superiority of these novel compounds, that they can be especially tailored for specific systems, that is, their compatibility with a given system, be it aqueous or organic, can be optimized, and even structural elements can be matched, by selecting the proper nonionic derivative for the synthesis. 30

Synthesis of these novel surfactants is conveniently carried out in two steps: the first involves the ring-opening reaction of maleic anhydride with a polyether, polyester diol, diamine or polysiloxane derivative which may be either an alcohol or a primary amine [and may also contain hydrophobic segments such as aliphatic or aromatic hydrocarbon groups or polypropylene oxide segments]. The second step consists of a base catalyzed addition of a perfluoroalkyl substituted thio onto the maleic double bond, carried out in a suitable solvent or in bulk. 35

The novel surfactants contain a carboxy group and are soluble in dilute mineral acid solution and thus behave like non-ionic surfactants. At base pH, the carboxy groups contribute to increased solubility. 40

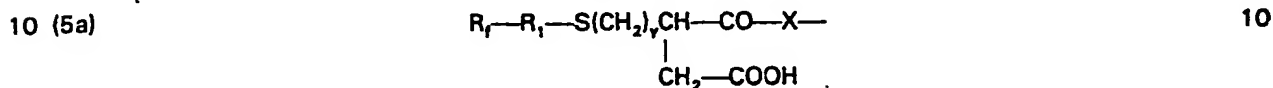
This invention is directed to the perfluoroalkyl substituted half esters and amides having the formula



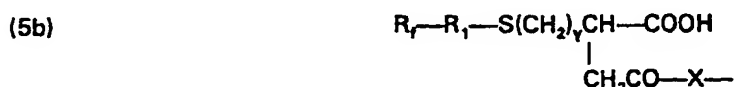
45 or



wherein  $R_f$  is straight or branched chain perfluoroalkyl of 4 to 18 carbon atoms or said perfluoroalkyl substituted by perfluoroalkoxy of 2 to 6 carbon atoms,  $R_1$  is branched or straight chain alkylene of 1 to 12 carbon atoms, alkylene thioalkylene of 2 to 12 carbon atoms, alkyleneoxyalkylene of 2 to 12 carbon atoms or alkyleneiminoalkylene of 2 to 12 carbon atoms where the nitrogen atom contains as a third substituent, hydrogen or alkyl of 1 to 6 carbon atoms, X is oxygen or NH, y is 1 or zero, Q is a polyether or polyester diradical moiety having a molecular weight of 300 to 5000 or a polysiloxane having 5 to 80 repeating units, and A is hydrogen, hydroxyl, amino, alkoxy of 1 to 21 carbon atoms, phenoxy, alkylphenoxy of 7 to 24 carbon atoms, preferably of 7 to 20 carbon atoms, dialkylamino where each alkyl has 1 to 18 carbon atoms or the group of the formula



or



wherein  $R_f$ ,  $R_1$ , X and y have the indicated meanings.

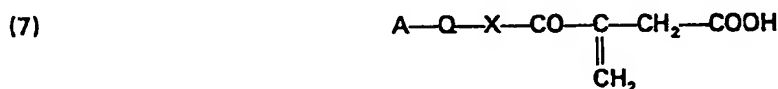
The phenoxy radical (A) may contain one or more than one alkyl substituent, and is e.g. methylphenoxy, octylphenoxy, nonylphenoxy or dinonylphenoxy. 15

Preferably  $R_f$  is a straight or branched chain perfluoroalkyl of 4, preferably 6 to 12 carbon atoms,  $R_1$  is alkylene of 1 to 6 carbon atoms and most preferably ethylene, y is zero, Q is a polyalkylene oxide moiety having from 10 to 50 repeating units, such as polyethylene oxide, A is hydroxyl, amino, methoxy or alkylphenoxy of 7 to 15 carbon atoms and X is  $-O-$  or  $-NH-$  most preferably  $-O-$ .

20 The compounds of this invention can be conveniently prepared by a two-step method. The first step consists of a condensation reaction of an alcohol, diol, amine or a diamine of the formula  $A-Q-X-H$ , wherein A, Q, and X have the indicated meanings with maleic or itaconic anhydride to yield intermediate of formulae



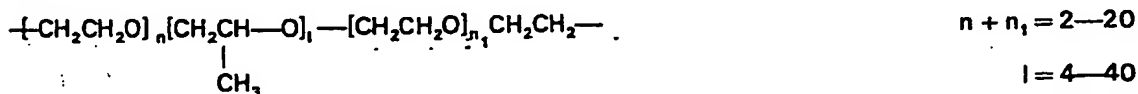
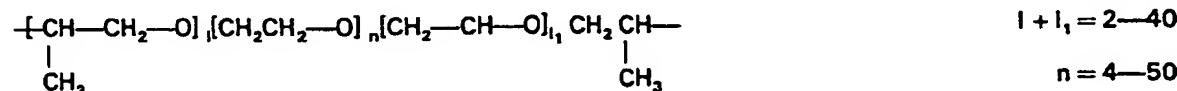
25 or 25



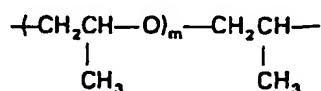
Said intermediates can also be prepared through transesterification with lower-alkyl esters of maleic, fumaric or itaconic esters such as mono- and dimethyl esters of maleic fumaric or itaconic acids. The most useful starting material for the intermediate of formula (6) is maleic anhydride. Methyl-maleic acid and chloromaleic acid derivatives can be used in the process of this invention, but give 30 unpractically low yields of the desired end-product.

In the second step a base catalyzed addition reaction of a perfluoroalkyl alkylene thiol of the formula  $R_f-R_1-SH$  and an intermediate of formula (6) or (7) is carried out.

The group Q is a polyether, polyester or siloxane diradical. Following are illustrative examples of 35 polyether diradicals:



40  $R^3 = \text{alkyl of } 1-18 \text{ C-atoms}$  40



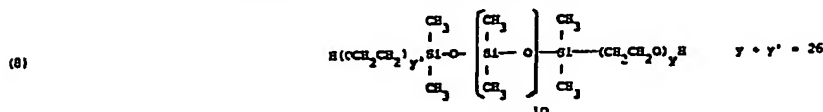
$$m = 6-50$$



$$x = 2-50$$

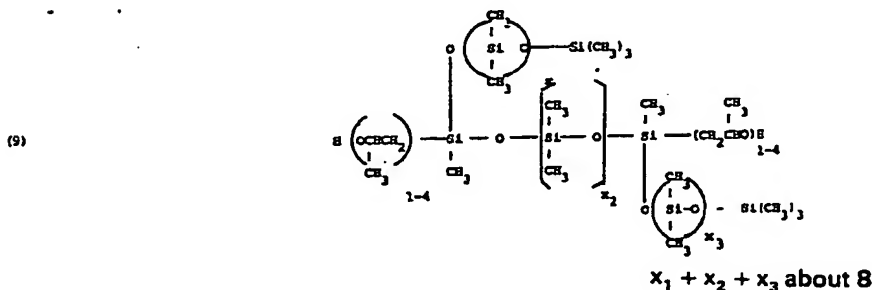
Examples of polyester-diol diradicals are those derived from diacids and diols, for instance alkylene glycol polyadipate, polysebacate, polyisophthalate, polyorthophthalate, polymaleate, polyglutarate and the like; such polyester diols may be based on a mixture of several diols and diacids and are commercially available as polyurethane prepolymers in a molecular weight range from 400—5000.

Examples of polysiloxanes are such of formulae



10 or

10



Examples of the alcohols, diols and amines useful in the preparation of intermediates (6) and (7) are listed below:

- polyethylene oxide, MW 200—5000, preferably 400—2000;
- 15 — polypropylene oxide, MW 200—5000, preferably 400—2000;
- methoxy polyethylene oxide, MW 400—25000, preferably 400—2000;
- poly-tetramethylene oxide, MW 3000—6000;
- poly(ethylene-co-propylene oxide) block polymers, such as polypropoxy-(10—50) repeating units)-bispolyethoxy-(10—20) diol or polyethoxy-(10—50)-bis-polypropoxy (10—50)-diol;
- 20 — ethoxylated alkyl phenol where alkyl is octyl or monyl and the ethoxylated group contains from 5 to 50 ethylene oxide units,
- ethoxylated primary and secondary amines of 8 to 20 carbons,
- ethoxylated fatty acids and amides of 8 to 20 carbons, alkoxyated alcohols and diols of 8 to 20 carbons, bis(2-amino propyl)ethers of polyethylene oxide and polypropylene oxide,
- 25 — Siloxane diols and triols, ethoxylated mercaptans of 8 to 20 carbons.

The perfluoroalkyl thiols employed in the preparation of the compounds of this invention are well known in the prior art. For example, thiols of the formula  $R_f\text{---R}'\text{---SH}$  have been described in a number of U.S. patents including 2,894,991; 2,961,470; 2,965,677; 3,088,849; 3,172,190; 3,544,663 and 3,655,732.

30 Thus, U.S. Patent 3,655,732 discloses mercaptans of formula

30



where

$R'$  is alkylene of 1 to 16 carbon atoms and  $R_f$  is perfluoroalkyl and teaches that halides of formula  $R_f\text{---R}'\text{---hal}$  are well known; reaction of  $R_f\text{I}$  with ethylene under free-radical conditions gives  $R_f(\text{CH}_2\text{CH}_2)_n\text{I}$  while reaction of  $R_f\text{CH}_2\text{I}$  with ethylene gives  $R_f\text{CH}_2(\text{CH}_2\text{CH}_2)_n\text{I}$  as is further taught in U.S. Patents 3,088,849; 3,145,222, 2,965,659 and 2,972,638.

35

U.S. Patent 3,655,732 further discloses compounds of formula



where

40  $R'$  and  $R''$  are alkylene of 1 to 16 carbon atoms, with the sum of the carbon atoms of  $R'$  and  $R''$  being not greater than 25;  $R_f$  is perfluoroalkyl of 4 through 14 carbon atoms and  $X$  is  $\text{---S---}$  or  $\text{NR}'''$

40

U.S. Patent 3,544,663 teaches that the mercaptans of formula



where

$R_f$  is perfluoroalkyl of 5 to 13 carbon atoms, can be prepared by reacting the perfluoroalkyl alkylene iodide with thiourea or by adding  $H_2S$  to a perfluoroalkyl substituted ethylene ( $R_f-CH=CH_2$ ), which in turn can be prepared by dehydrohydrogenation of the halide  $R_f-CH_2CH_2-hal$ . 5

The reaction of the iodide  $R_f-R^1-I$  with thiourea followed by hydrolysis to obtain the mercaptan  $R_f-R^1-SH$  is the preferred synthetic route. The reaction is applicable to both linear and branched chain iodides. Many useful perfluoroalkoxyalkyl iodides are described in U.S. Patent 3514487 of general formula 10



where

$m$  is 1—3.

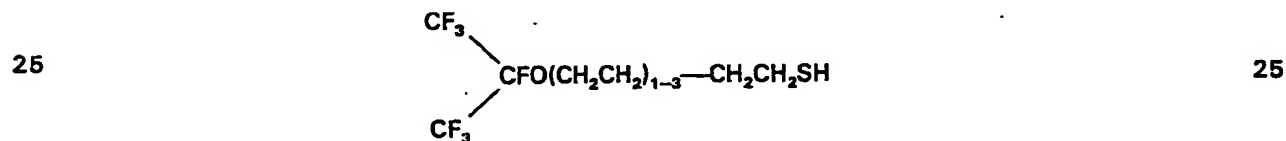
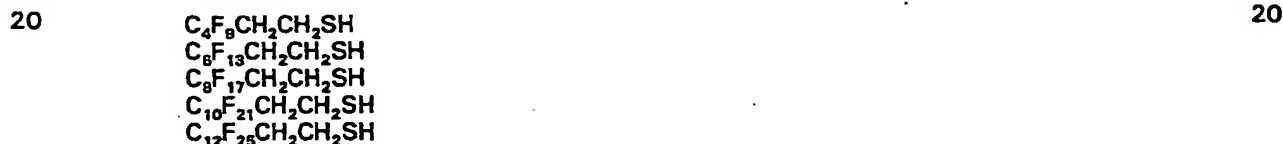
Particularly preferred herein are the thiols of formula



where

$R_f$  is perfluoroalkyl of 6 to 12 carbon atoms. These  $R_f$ -thiols can be prepared from  $R_fCH_2CH_2I$  and thiourea in very high yield.

Illustrative examples of preferred perfluoroalkylalkylenethiols are:



Especially preferred perfluoroalkylalkylenethiols are:



and mixtures thereof.

Synthesis of the novel nonionic surfactants is most conveniently carried out in two steps: the first step consists of reacting the cyclic anhydride, most commonly maleic anhydride, with the hydroxy or aminosubstituted nonionic compound either in bulk or in a common dry and aprotic solvent; useful solvents include ketones, such as acetone and methylethyl ketone; ethers, such as diethylether or ethylene glycol — dimethylether, or tetrahydrofuran; esters, such as ethyl acetate or methyl cellosolve acetate; amides, such as dimethylformamide or N-methyl pyrrolidone. While amines react rapidly at room temperature, hydroxy compounds have to be heated for several hours to 50—100°C. The second step involves addition of the perfluoroalkyl alkylene thiol to the intermediate maleic half ester or half amide in the presence of basic catalysts, such as triethylamine, pyridine, or tetramethyl ammonium hydroxide. Addition of the thiol to the mixture often leads to heterogeneous, 2-phase system, which will turn into a homogeneous solution, as the reaction proceeds. This reaction step is preferably carried out between 30 and 75°C under a nitrogen blanket and with good stirring. 35 40

The compounds of this invention can also be prepared by reversing the order of the reaction described above; that is, first carry out the base catalyzed addition of a perfluoro substituted thiols to maleic anhydride followed by the ring opening with the hydroxy or amino substitute nonionic compound. 45

Such fluorochemical surfactants are useful to improve or impart properties such as: wetting, penetration, spreading, levelling, foam stability, flow properties, emulsification, dispersion, and oil and water repellency. Based on these unique properties are numerous applications, some of which follow. 50  
 Although applications are suggested for a particular use area, the general applicability of each concept is inferred for other applications.

**PLASTICS AND RUBBER INDUSTRY**

- Emulsifying agent for polymerization, particularly fluoromonomers
- As a latex stabilizer
- To aid in the preparation of agglomerates of powdered fluorocarbon polymers
- 5 — In synergistic mixtures with hydrocarbon surfactants to wet low energy surfaces including natural and synthetic rubbers, resins, plastics 5
- As an adjuvant for foam applications and as foaming agents to aid in leak detection
- As a foam additive to control spreading, crawling, edge buildup
- As mould release agents, for silicones, etc.
- 10 — In refractory processes 10
- As an anti-mist film former
- Additive for elimination of trapped air in plastic laminates
- Wetting agent for resin molds for definition, strength
- Hot-melt additive for oil and grease repellency
- 15 — Resin additive for improved wetting of and bonding with fillers 15
- Flow modifier for extruding hot melts: spreading, uniformity, anti-cratering
- Adjuvant for resin etchant
- Mold release agent, demoulding agent
- Retarder for plasticizer migration or evaporation
- 20 — Internal antistatic agent for polyolefins 20
- Antiblocking agent for polyolefins

**PETROLEUM INDUSTRY**

- As a film evaporation inhibitor for gasoline, jet fuel, solvents, hydrocarbons
- In extreme pressure lubricants

- 25 **TEXTILE AND LEATHER INDUSTRIES** 25
- Soil release and soil proofing agent
- Oil/water repellent textile and leather treatment
- Wetting agent to improve coverage and penetration of pores of substrates
- Anti-foaming agent in textile treatment baths
- 30 — Wetting agent for finish-on-yarn uniformity 30
- Penetrating agent for finishes on tow, heavy denier fibers
- Emulsifying agent/lubricant for fiber finishes
- Cleaner/metal treating agent for polymerization equipment
- Flow modifier for spinning of hot melts, solutions
- 35 — Additive for fabric finishes for spreading, uniformity 35
- Wetting agent for dyeing
- Penetration aid for bleaches
- Wetting agent for binder in nonwoven fabrics

**PAINT, PIGMENT AND FINISHING INDUSTRIES**

- 40 — Levelling, anti-catering adjuvant for finishes and paints 40
- Adjuvant for control of soiling
- Agent to control differential evaporation of solvents
- Levelling agent for floor waxes
- Adjuvant for waxes to improve oil and water repellency
- 45 — Adhesion improver for oily or greasy surfaces 45
- To combat pigment flotation problems
- Improver for automotive finishes, based on water-based coatings in which the pigments are rendered non reactive
- Pigment grinding aid to promote wetting, dispersion, color development
- 50 — Foam generator substance for the application of dyes, inks 50
- Electrolytic conversion coatings

**MINING AND METALWORKING INDUSTRIES**

- In cleaning agents for property improvement
- Additive for solvent cleaning
- 55 — Additive for metal pickling baths to increase bath life and acid runoff 65
- Additive for chrome electroplating: surface tension reduction, foaming
- Additive for soldering flux, especially for electronic circuitry
- Protective agent for coatings (tarnish resistance, grease repellency)
- Corrosion inhibitor
- 60 — Additive for etchant solution for improved definition 60
- Plastic emulsate and silicon etchant technology

— In soldering flux for microelectronics to reduce foaming	
— In chemical roughing agent solutions, prior to galvanization	
— As a colloidal dispersion aid for magnetic solids	
— Protective coatings for aluminum and as an anti-blocking agent	
5 — Wetting agent for leaching copper ores and as a fresh flotation agent	5
— To promote ore wetting and quicker breaking of the protective oxide layer	
<b>PHARMACEUTICAL INDUSTRY</b>	
— Improve the properties and penetration of anti-microbial agents	
— Improve the properties of biochemicals, biocides, algicides, bactericides, and bacteriostats	
10 — Improve the strength, homogeneity, and reduce the permeability of encapsulated materials	10
— Emulsifying fluorochemical blood substituted	
<b>AGRICULTURE AND FORESTRY</b>	
— Wetting agent for herbicides, fungicides, weed killers, hormone growth regulators, parasiticides, insecticides, germicides, bactericides, nematocides, microbiocides, defollients and fertilizers	
15 — As an ingredient in chemosterilents, insect repellents and toxicants	15
— For wettable powder pesticides and chemical powders	
— Corrosion inhibitor for chemical applicators	
— Wetting agent for foliage	
— Wetting additive for live stock dips, or to wet sheep skins during desalination	
20 — Wetting adjuvant for manufacture of plywood veneer	20
— Penetrant for preservative impregnation	
— Pulping aid	
— For cleaning tubes in paper making, dyeing	
— Grease/oil repellents for paper	
25 <b>FIRE FIGHTING</b>	25
— Wetting agent for fighting forest fires	
— Ingredient of AFFF (aqueous film forming foams) extinguishing agents	
— Component of fluoroprotein foams	
— Additives to dry chemical extinguishing agents	
30 — Agent in aerosol-type extinguishers	30
— Wetting agent for sprinkler water	
<b>AUTOMOTIVE, BUILDING MAINTENANCE AND CLEANING</b>	
— Wetting agent for cleaning compositions	
— Additive for alkaline cleaners	
35 — Glass cleaner	35
— Wetting agent for automobile waxes	
— Adjuvant to improve oil/water repellency of wax	
— Lubricant/corrosion inhibitor for antifreeze	
— Rinse-aid for car washes	
40 — In dry cleaning compositions and solvent cleaners, for water displacement and foaming. May improve soil suspension and decrease redeposition	40
— Foaming agents for pipe cleaning	
— Anti-mist film foamer for glass and plastics	
— In foams for dust suppression	
45 — For acidic concrete cleaners	45
— Bubble foamer for air tracing, in ventilating systems	
<b>HOUSEHOLD, COSMETIC AND PERSONAL PRODUCTS</b>	
— Rinse-aid for dishwashing	
— Liquid polishing compositions	
50 — Floor polish leveling agent	50
— Additive for alkaline oven cleaners	
— Synergistic improver for disinfectants	
— Carpet cleaners	
— Synergistic wetting agent in detergent formulations	
55 — Additive for protective coatings on metals (tarnish resistance, grease resistance)	55
— Gloss and antistatic improver	
— Hair shampoo ingredient	
— Shaving foam ingredient	
— Oil and water repellent cosmetic powders ingredient	
60 — Ingredient of lotions or creams for skin or hair	60
— Ingredient of skin protection creams	

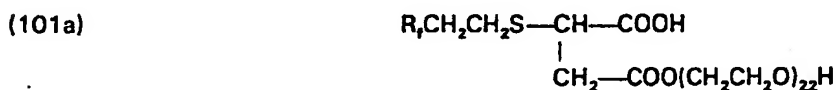
## PHOTOGRAPHY AND GRAPHIC ARTS.

- Printing ink additive for ink flow and levelling, both aqueous and solvent based
- Wetting agent for writing inks
- To combat pigment flooding and flotation in printing inks
- 5 — To form ink repellent surfaces for waterless lithoplates, or electrographic coatings 5
- Prevent reticulation of gelatin layers and improve uniformity
- Assist in film drying
- Improve film coatings and reduce "contraction flecks"
- Wetting, levelling, anti-cratering assist agent
- 10 — Surfactant for developer solutions 10
- Photoemulsion stabilizer
- Prevent photo-lubricant agglomeration
- Coating aid in the preparation of multiple layer film elements
- Antistatic wetting agent for film coatings
- 15 — Antifogging agent for films 15
- Bonding agent for fillers and fluoropolymer films
- In coatings for nematic liquid crystal cells

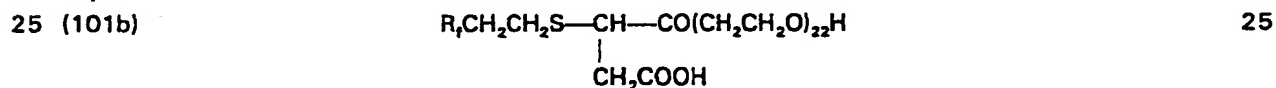
The examples below are presented for illustrative purposes only and do not limit the scope of the invention. In the examples the surface tension was measured with a DuNouy tensiometer at 0.1% concentration in water at 25°C. 20

## EXAMPLE 1

Synthesis of compounds of the formulae



and



2.5 g (0.0255 mol) maleic anhydride in 2.5 g methyl-ethyl ketone were added to 25 g (0.025 mol) polyethylene oxide of molecular weight 1000 (number of ethyleneoxide units between about 15 and 30) and stirred for 12 hours at 75°C under a nitrogen blanket. At this time, infrared analysis showed no anhydride bands left at 1780 cm<sup>-1</sup> and 1850 cm<sup>-1</sup>.

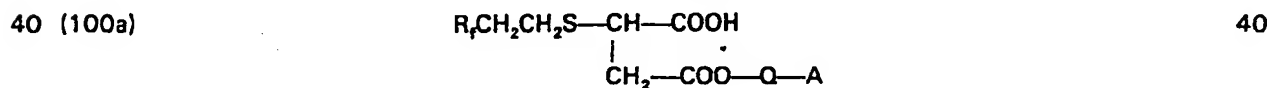
30 11.8 g perfluoroalkyl-ethylmercaptan\* (0.025 mol) of average molecular weight 478 were added together with 0.2 g triethylamine as catalyst (0.002 mol) and the mixture stirred for 12 hours at 50°C. The initially opaque white mixture turned clear after three hours. The clear solution was dried in vacuo at 80°C for 5 hours. The product is a soft wax which is soluble in water. 30

35 Elemental Analysis: C H F 35  
Calc.: 47.6 6.3 19.7  
Found: 46.0 6.3 18.1

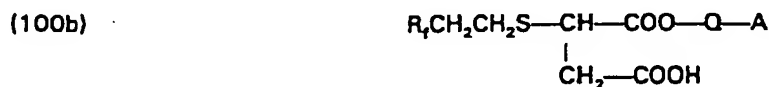
\*The perfluoroalkyl moiety R<sub>f</sub> has a distribution of 27% (± 5%) C<sub>6</sub>, 50% (± 5%) C<sub>8</sub> and 23% (± 5%) C<sub>10</sub>.

## EXAMPLES 2—12

Using the procedure of Example 1, compounds of structure



and



were prepared with hydroxy compounds listed in Table 1.

Surface tension was measured for each example, including Example 1 for a 0.1% solution in water.



TABLE 1

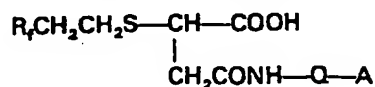
Example	Nonionic Moiety HO—Q—A	Elemental 1) Analysis			$\gamma_s \left( \frac{\text{Dynes}}{\text{cm}} \right)$ 0.1% in H <sub>2</sub> O
		C	H	F	
1	Polyethyleneoxide MW 1000	47.6 46.0	6.3 6.3	19.7 18.1	27.1
2	N-stearyl-dipolyethoxy (15) amine	48.9 50.9	6.9 7.5	20.6 19.4	28.0
3	Polypropoxy (31) bispolyethoxy (26) diol	54.3 54.7	8.4 9.4	9.0 6.7	23.7
4	Polyethoxy (23) bispolypropoxy (29) diol	53.6 53.7	8.6 8.3	9.9 8.3	21.2
5	Methoxy polyethylene oxide	43.3 44.5	5.8 6.3	23.4 20.4	19.7
6	Nonylphenoxy polyethylene oxide	49.3 50.7	6.6 7.1	19.2 16.2	25.9
7	Octylphenoxy polyethylene oxide	50.2 50.2	7.1 7.2	14.5 14.3	18.4
8	Polysiloxane diol	41.1 40.6	7.0 6.9	11.1 10.4	28.4
9	Polypropylene oxide	49.5 49.7	7.1 7.3	19.9 18.7	not soluble
10	Poly-n-butylene oxide	51.4 54.0	7.2 7.9	19.7 17.8	not soluble
11	Polysiloxane triol; MW 6000	—	—	12 11.7	not soluble
12	Polysiloxane diol; MW 800	—	—	31.8 31.9	not soluble

1) Calculated  
Found

## EXAMPLES 13—16

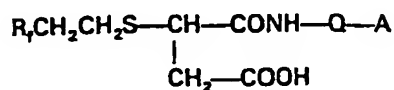
Using the procedure of Example 1, compounds of structure:

(200a)



5 and

(200b)



5

TABLE 2

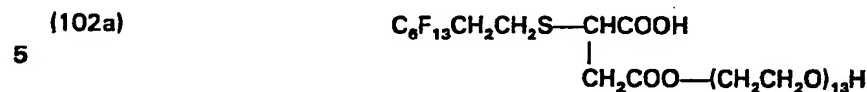
Example		Elemental Analysis <sup>1)</sup>			$\gamma_s$ [ $\frac{\text{Dynes}}{\text{cm}}$ ] 0.1%
		C	H	F	
13	Polyoxdiamine $\overline{\text{MW}}$ 600 2) (ED)	45.2 44.5	6.4 6.4	20.3 21.0	31.3
14	Polyoxdiamine $\overline{\text{MW}}$ 1000 (ED)	42.1 43.7	5.6 6.0	27.4 25.4	31.3
15	Polyoxdiamine $\overline{\text{MW}}$ 2000 (ED)	48.8 49.5	7.5 8.0	12.0 11.0	36.0
16	Polypropylene oxide diamine (D)	53.9 54.7	8.4 8.8	12.0 11.7	not soluble

1) Calculated  
Found

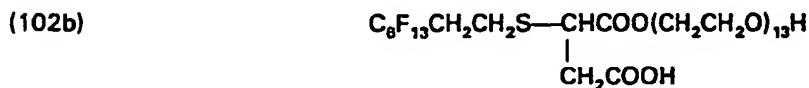
2) Bis-3-aminopropyl ethers of polyethylene oxide (ED) and polypropylene oxide (D)

## EXAMPLE 17

Reaction Products of Polyethyleneoxide 600, Maleic Anhydride and 1,1,2,2-Tetrahydroperfluorooctyl Mercaptan



and



Maleic anhydride (0.0255 moles, 2.5 g) dissolved in 10 g acetone was added to Polyethyleneoxide (MG = 600) (0.0255 moles, 15.3 g) and stirred overnight with triethylamine catalyst (2.5 mole %).

Infrared spectrum showed no anhydride bands left at  $1780\text{ cm}^{-1}$  and  $1850\text{ cm}^{-1}$ .

1,1,2,2-tetrahydroperfluorooctyl mercaptan (0.0255 moles, 9.64 g) was added and the reaction was stirred at room temperature for 2 days before TLC showed no unreacted mercaptan. The clear solution was dried under vacuum to give 23.0 g of a clear white oil (83.8% yield).

Infrared analysis was consistent for the structure.

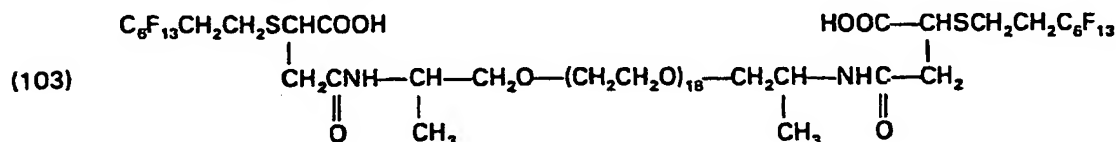
	C	H	F
Calc.:	42.84	5.69	22.93
Found:	42.56	5.84	22.08

Surface tension of a 0.1% solution in water was

27.7  $\frac{\text{[dynes]}}{\text{cm}}$

## EXAMPLE 18

Reaction Product of bis-3-aminopropyl ether of polyethylene oxide (MW—1000), Maleic Anhydride and 1,1,2,2-Tetrahydroperfluorooctyl Mercaptan



5 and its isomer.

Maleic anhydride (0.0255 moles, 2.5 g) was added to bis-3-aminopropyl ether of polyethylene oxide (MW = 1000) (0.01275 moles, 11.86 g) in 10 g acetone and the reaction was stirred for 24 hours (IR) shows no anhydride bands at  $1780\text{ cm}^{-1}$  and  $1850\text{ cm}^{-1}$ .

1,1,2,2-tetrahydroperfluorooctyl mercaptan was added and the reaction was stirred overnight at 10 room temperature. TLC showed no traces of unreacted mercaptan.

The clear yellow solution was dried under vacuum to give 26.17 g of a clear yellow viscous oil (99.7% yield).

Infrared analysis was consistent for the structure.

Elemental analysis for  $\text{C}_{66}\text{H}_{102}\text{F}_{26}\text{N}_2\text{O}_{25}\text{S}$

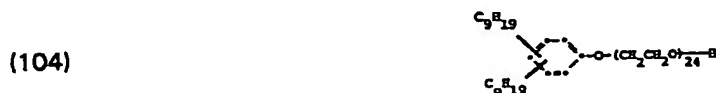
15		C	H	N	F	15.
	Calc.:	42.16	5.47	1.49	26.18	
	Found:	42.62	6.04	1.56	24.26	

A 0.1% solution in water together with 0.1%  $\text{C}_8\text{H}_{17}\text{C}_6\text{H}_5\text{O}(\text{C}_2\text{H}_4\text{O})_{10}$  had a surface tension of

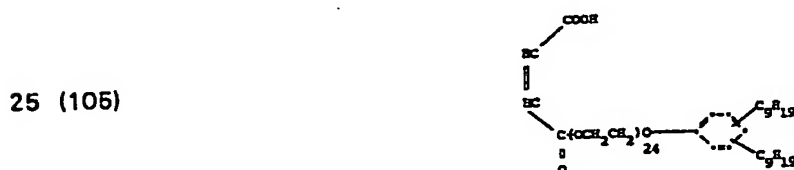
$$\frac{23.8 \text{ [dynes]}}{\text{cm}}$$

## 20 EXAMPLES 19 to 23

2.55 g of maleic anhydride and 2.55 g of sulfolane as solvent are added to 36.45 g of the dinonyl phenol of the formula

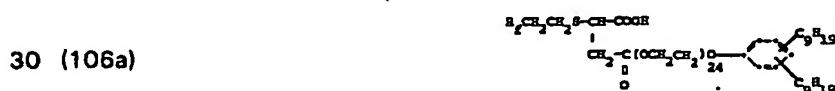


and stirred for 20 hours at  $60^\circ\text{C}$ , to form a reaction mixture containing a half ester of the formula



and its isomer.

To this reaction mixture there is then added 0.1 gram of triethylamine and 11.63 grams of  $\text{R}_f\text{CH}_2\text{CH}_2\text{SH}$  and a nitrogen blanket and the mixture stirred at  $60^\circ\text{C}$  for about 7 hours. The product has the formula



and



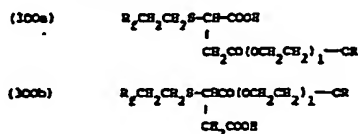
R<sub>f</sub> — distribution: 0.9% C<sub>18</sub>F<sub>37</sub>, 32.9% C<sub>18</sub>F<sub>35</sub>, 37.5% C<sub>18</sub>F<sub>33</sub>, 22.9% C<sub>18</sub>F<sub>31</sub>, and 5.3% C<sub>18</sub>F<sub>29</sub>


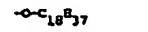



Examples 20 to 23 are prepared in the same manner.

Surface tension is measured for each sample for a 0.1% solution in water.

Table 3

Compounds of formula

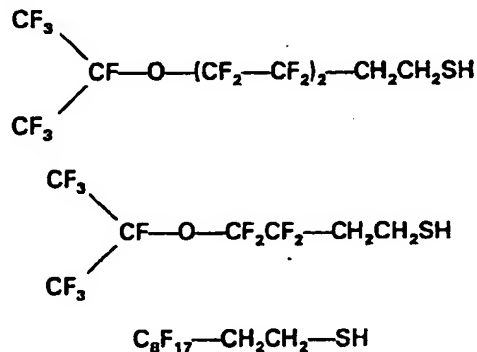


Example	Value of $\mu$	OR	Surface tension (Dynes/cm)
19	24		29.2
20	20		27.1
21	15		24.2
22 1)	20		26.3
23	5		24.5

1)  $R_1$ -distribution 25 %  $C_{18}H_{37}$ , 50 %  $C_{17}H_{35}$ , 25 %  $C_{16}H_{33}$ .

#### EXAMPLE 24

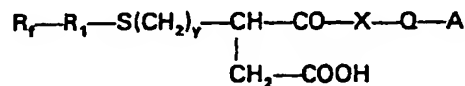
Example 1 is repeated using the following  $R_1$ -thiols:



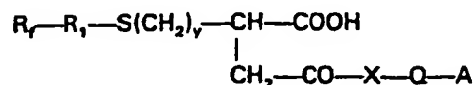
to give the corresponding water soluble surfactants.

#### 10 CLAIMS

1. Perfluoroalkyl substituted half esters and amides having the formula

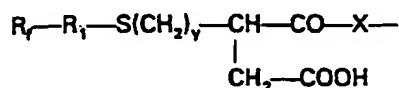


or

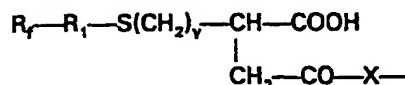


- 15 wherein  $R_1$  is straight or branched chain perfluoroalkyl of 4 to 18 carbon atoms or said perfluoroalkyl substituted by perfluoroalkoxy of 2 to 6 carbon atoms,  $R_2$  is branched or straight chain alkylene of 1 to 12 carbon atoms, alkylthioalkylene of 2 to 12 carbon atoms, alkyleneoxyalkylene of 2 to 12 carbon atoms or alkyleneiminoalkylene of 2 to 12 carbon atoms where the nitrogen atom contains as a third substituent, hydrogen or alkyl of 1 to 6 carbon atoms, X is oxygen or NH, y is 1 or zero, Q is a polyether
- 20 or polyester diradical moiety having a molecular weight of 300 to 5000 or a polysiloxane having 5 to 80

alkylphenoxy of 7 to 24 carbon atoms, dialkylamino where each alkyl has 1 to 18 carbon atoms, the group



or



wherein  $R_f$ ,  $R_1$ ,  $X$  and  $y$  have the indicated meanings.

2. A compound according to claim 1, wherein  $A$  is alkylphenoxy of 7 to 20 carbon atoms.

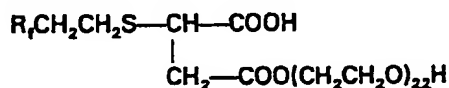
3. A compound according to claim 1 wherein  $R_f$  is a straight or branched chain perfluoroalkyl of 4 to 12 carbon atoms,  $R_1$  is alkylene of 1 to 6 carbon atoms,  $y$  is zero,  $Q$  is a polyoxyalkylene oxide having 10 to 50 repeating units,  $A$  is hydroxyl, amino, methoxy or alkylphenoxy of 7 to 24 carbon atoms, and  $X$  is  $-O-$  or  $-NH-$ .

4. A compound according to claim 1 wherein  $R_f$  is a straight or branched chain perfluoroalkyl of 6 to 12 carbon atoms and  $Q$  is a polyethylene oxide moiety.

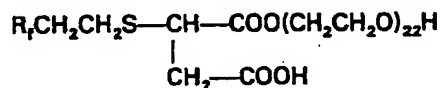
5. A compound according to claim 1 wherein  $R_f$  is a straight or branched chain perfluoroalkyl of 6 to 12 carbon atoms,  $R_1$  is ethylene,  $y$  is zero,  $X$  is oxygen and  $A-Q$  is derived from the group selected from polyethyleneoxide of MW 400—2000; polypropoxy-(having 10—50 repeating units)-bit-polyethoxy-(10—20) diol; polyethoxy-(10—50)-bis-polypropoxy-(10—50) diol; methoxy-polyethylene oxide of MW 400—2000; and nonylphenoxy polyethylene (5—50) oxide or octylphenoxy polyethylene (5—50) oxide.

6. A compound according to Claim 2 wherein  $A-Q$  is derived from a bis(2-aminopropylether) of polyethylene oxide of MW 400—2000 or polypropylene oxide of MW 400—2000.

7. A mixture of compounds according to Claim 1 having the formulae

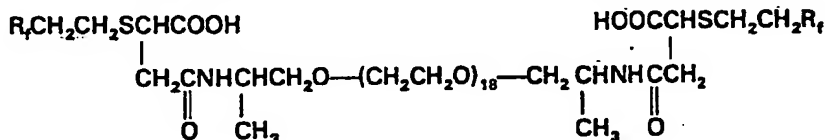


and



wherein  $R_f$  has a distribution of 27%  $C_6$ , 50%  $C_8$  and 23%  $C_{10}$ .

8. A mixture of compounds according to Claim 1 having the formula



and its isomer, wherein  $R_f$  has a distribution of 27%  $C_6$ , 50%  $C_8$  and 23%  $C_{10}$ .

9. Use of the compounds according to any one of claims 1 to 8 as surfactants.

10. A compound of the formula shown in claim 1 as described with particular reference to any one of the Examples 1 to 18 and 24.

11. A compound of the formula shown in claim 1 as described with particular reference to any one of the Examples 19 to 23.

12. Use of the compounds of the formula shown in claim 1 as described with particular reference to any one of the Examples 1 to 18 and 24.

13. Use of the compounds of the formula shown in claim 1 as described with particular reference to any one of the Examples 19 to 23.